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13. ABSTRACT (Maximum 200 words)  Superhard, dielectric and optoelectronic materials in the Si-C-Al-N, Si-B-O-N and Zr-B/Ga-N systems were prepared as thin films via novel CVD and MBE routes. SiC and AlN, normally insoluble in each other below 2000 °C are combined to form single phase SiCAIN by gas source MBE of SiH <sub>3</sub> CN and Al atoms at 750°C. The growth of epitaxial material takes place on 6H SiC and Si(111). Commensurate heteroepitaxy between Si(111) and SiCAIN is facilitated by the presence of a crystalline (Si-O-Al-N) oxide at the Si interface. The bandgap of SiCAIN is 3.2 eV and average hardness is 25 Gpa. Superhard metal borides such as ZrB <sub>2</sub> and ternary analogs have been grown as perfectly epitaxial layers on Si(111). These materials in turn are used as totally reflective and lattice-matched buffer layers for integration of light emitting nitrides (GaN and AlGaN) with Si. UHV-CVD growth of single-phase Ge <sub>1-x-y</sub> Si <sub>x</sub> Sn <sub>y</sub> semiconductors is conducted for the first time on Si(100). These materials exhibit tunable band gaps and possess lattice constants above and below that of Ge. The fabrication of Ge <sub>1-x-y</sub> Si <sub>x</sub> Sn <sub>y</sub> makes it possible to decouple strain and band gap engineering to achieve unique structures that lead to novel photonic devices based entirely on group IV materials (covering a wide range of operating wavelengths in the IR). Growth of random Ge <sub>1-x</sub> Sn <sub>x</sub> alloys and related ordered structures has been achieved directly on Si(100). Optical characterizations show a Ge like band structure. The band gaps and critical point energies are reduced monotonically with Sn content indicating that band gap engineering has been obtained in this system.				
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**Final Technical Report**

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"Synthesis of Thin Films and Coatings Based on Light Elements"

**Principal Investigators**

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**Publications Acknowledging ARO Support**

- 1 J. Taraci, S. Zollner, M. R McCartney, J. Menendez, M. A. Santana-Aranda, D. J. Smith, Arne, Haaland, A. V. Tutukin, G. Gundersen, G. Wolf, and J. Kouvetakis, "Synthesis of Silicon-Based Infrared Semiconductors in the Ge-Sn System Using Molecular Chemistry Methods" *J. Am. Chem. Soc.* **123(44)**, 10980-10987, (2001).
- 2 M. Chirita, H. Xia, R. Sooryakumar, J.B. Tolle, V.M. Torres, B.J. Wilkens, D.J. Smith, J. Kouvetakis and I.S.T. Tsong, "Elastic properties of nanocrystalline zirconium-silicon-boron thin films", *J. Appl. Phys.* **89**, 4349-4353 (2001).
- 3 R. Roucka, J. Tolle, D.J. Smith, P. Crozier, I.S.T. Tsong and J. Kouvetakis, "Low-temperature growth of SiCAlN films of high hardness on Si(111) substrates", *Appl. Phys. Lett.* **79**, 2880-2882 (2001).
- 4 Darrick Williams, B. Pleune, C. Leinenweber, and J. Kouvetakis "Synthesis and structural properties of stoichiometric framework C-N compounds of Be, Mg, Al, and Ti", *J. of Solid State Chem.* **159**, 244-250 (2001).
- 5 J. Kouvetakis, Cory Steffek, Levi Torrison, Jeff McMurran and J. Hubbard, "Synthesis of new azidoalanes with heterocyclic molecular structures", *Main Group Metal Chemistry* 2001, **24** (2) 77-84.
- 6 R. Roucka, J. Tolle, A.V.G. Chizmeshya, P.A. Crozier, C.D. Poweleit, D.J. Smith, I.S.T. Tsong and J. Kouvetakis, "Low-temperature epitaxial growth of the quaternary wide band gap semiconductor SiCAlN", *Phys. Rev. Lett.* **88**, 206102 (2002).
- 7 J. Tolle, R. Roucka, P. Crozier, A. Chizmeshya, I.S.T. Tsong and J. Kouvetakis, "Growth of SiCAlN on Si crystalline oxide interfaces", *Appl. Phys. Lett.* **81**, 2181-2183 (2002).
- 8 J. Taraci, S. Zollner, M.R. McCartney, J. Menendez, D.J. Smith, J. Tolle, M. Bauer, E. Duda, N.V. Edwards and J. Kouvetakis, "Optical vibrational and structural properties of Ge<sub>1-x</sub>Sn<sub>x</sub> alloys by UHV-CVD", *Mat. Res. Soc. Symp. Proc.* **602**, 1141-1146 (2002).
- 9 M. Bauer, J. Taraci, J. Tolle, A.V.G. Chizmeshya, S. Zollner, J. Menendez, D.J. Smith and J. Kouvetakis, "Ge<sub>1-x</sub>Sn<sub>x</sub> semiconductors for band-gap and lattice engineering", *Appl. Phys. Lett.* **81**, 2992-2994 (2002).
- 10 L. Torrison, J. Tolle, D.J. Smith, J. Menendez, C.D. Poweleit and J. Kouvetakis, "Morphological and optical properties of Si nanostructures imbedded in SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> films grown by single-source CVD", *J. Appl. Phys.* **92**, 7475-7480 (2002).
- 11 J. Tolle, R. Roucka, A.V.G. Chizmeshya, P.A. Crozier, D.J. Smith, I.S.T. Tsong and J. Kouvetakis "Novel synthetic pathways to wide bandgap semiconductors in the Si-C-Al-N system", *Solid State Sciences* **4**, 1509-1519 (2002).
- 12 L. Torrison, J. Tolle, J. Kouvetakis, S.K. Dey, D. Gu, I.S.T. Tsong and P.A. Crozier, "Stoichiometric and non-stoichiometric films in the Si-O-N system: mechanical, electrical and dielectric properties", *Mat. Sci. Eng. B* **97**, 54-58 (2003).
- 13 R. Roucka, J. Tolle, A.V.G. Chizmeshya, P.A. Crozier, C.D. Poweleit, D.J. Smith, J. Kouvetakis and I.S.T. Tsong, "Epitaxial growth of the pseudo-binary wide band gap semiconductor SiCAlN", *Appl. Surf. Sci.* **212/213**, 872-878 (2003).
- 14 L. Torrison, J. Tolle, I.S.T. Tsong and J. Kouvetakis, "Growth and optical properties of epitaxial GaN films on Si(111) using single-source molecular beam epitaxy", *Thin Solid Films* **434**, 106-111 (2003).
- 15 J. Tolle, R. Roucka, I.S.T. Tsong, C. Ritter, P.A. Crozier, A.V.G. Chizmeshya and J. Kouvetakis, "Epitaxial growth of group III nitrides on silicon substrates via a reflective lattice-matched zirconium diboride buffer layer", *Appl. Phys. Lett.* **82**, 2398-2400 (2003).

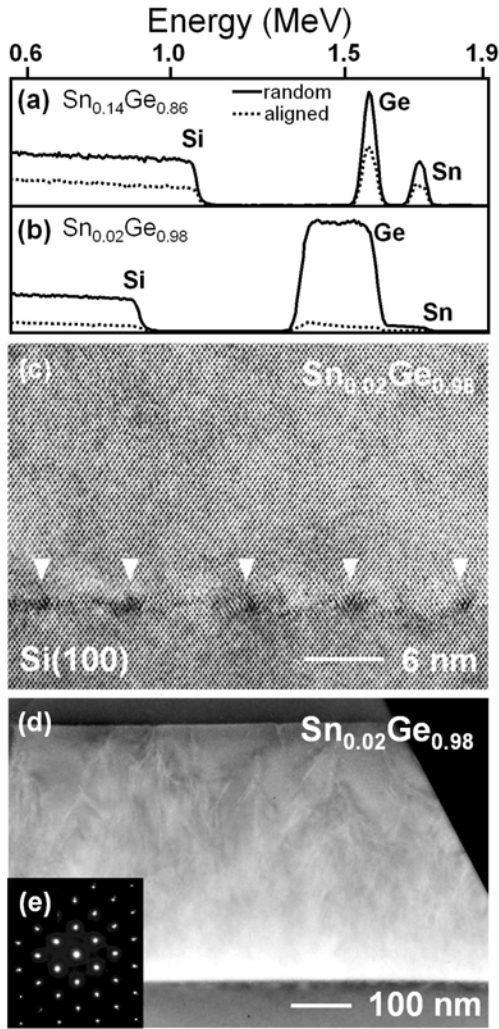
16. M.R. Bauer, J. Tolle, A.V.G. Chizmeshya, S. Zollner, J. Menendez and J. Kouvetakis, "New Ge-Sn materials with adjustable bandgaps and lattice constants", *Mat. Res. Soc. Symp. Proc.* **744**, 49-54 (2003).
  17. A. Chizmeshya, M. Bauer, J. Kouvetakis, "Experimental and theoretical studies of deviations from Vegard's law in the  $\text{Ge}_{1-x}\text{Sn}_x$  system", *Chem. Mater* **15**, 2511-19 (2003).
  18. C.S. Cook, S. Zollner, M. Bauer, J. Kouvetakis, J. Menendez, and J. Tolle, "Optical constants and interband transitions of  $\text{Ge}_{1-x}\text{Sn}_x$  alloys ( $x < 0.2$ ) grown on Si, Thin Solid Films (in press **2004**).
  19. "Synthesis of highly coherent SiGe and  $\text{Si}_4\text{Ge}$  nanostructures by single-source molecular beam epitaxy of  $\text{H}_3\text{SiGeH}_3$  and  $\text{Ge}(\text{SiH}_3)_4$ ", C.W. Hu, J.L. Taraci, J. Tolle, M.R. Bauer, P.A. Crozier, I.S.T. Tsong and J. Kouvetakis, *Chem. Mater.*, (2003), **15(19)**, 3569-3572
  20. "Tunable bandstructure in diamond cubic tin-germanium alloys grown on silicon substrates", Matthew Bauer, J. Kouvetakis, D.J. Smith and Jose Menendez, *Solid State Communications* . **127**, 355-359, (2003).
  21. "Synthesis of ternary Si-Ge-Sn semiconductors on Si(100) via  $\text{Sn}_x\text{Ge}_{1-x}$  buffer layers" Matthew Bauer, Cle Ritter, Peter Crozier, J. Menendez, Jie Ren, and J. Kouvetakis *Applied Physics Letters* **83 (9)**, 216-2165 (2003).
  22. "GeSn superstructured materials for Si-based optoelectronic technology". Matthew Bauer, Peter Crozier, A.V.G. Chizmeshya and J. D. Smith and J. Kouvetakis *Applied Physics Letters* **83**, 3489-3491, (2003).
  23. "Structural and optical properties of  $\text{Sn}_x\text{Si}_y\text{Ge}_{1-x-y}$  alloys" Pavan Aella, C. Cook, J. Tolle, S. Zollner, A.V.G. Chizmeshya and J. Kouvetakis, *Applied Physics Letters* **84**, 888-890, (2004).
  24. "Scaling law for the compositional dependence of Raman frequencies in GeSi and SnGe alloys" Shiu Fai Li, Matthew R. Bauer, José Menéndez, and John Kouvetakis, *Appl. Phys. Lett.* **84**, 867-869, (2004)
- 

### Patents Arising from ARO Support

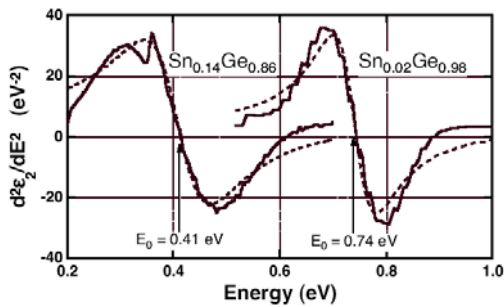
- 1 "Novel compositions of matter and methods of depositing pure thin films of GaN semiconductors", J. Kouvetakis and J. McMurran, **US Patent No 6,207,844**, (2001).
  - 2 "Low temperature epitaxial growth of quaternary wide bandgap semiconductors", J. Kouvetakis, I.S.T. Tsong, R. Roucka and J. Tolle. U.S. Patent application serial number 09/981,024; filing date 10/16/01. International Patent application serial number PCT/US02/33134; filing date 10/16/02.
  - 3 "Synthesis of superhard dielectric materials in the Si-B-N-O and Si-B-C-N systems", J. Kouvetakis, J. Tolle, I.S.T. Tsong and L. Torrison. International Patent application serial number PCT/US02/33124; filing date 10/11/02.
  - 4 "Active electronic devices based on GaN and its alloys grown on silicon substrates with buffer layers of SiCAlN", I.S.T. Tsong, J. Kouvetakis, J. Tolle and R. Roucka. U.S. Provisional Patent application serial number 60/410,859; filing date 9/13/02. Non-provisional US and PCT patent submitted 2/2004
  - 5 "Epitaxial growth of Group III nitrides on silicon substrates via a reflective lattice-matched zirconium diboride buffer layer", J. Kouvetakis, I.S.T. Tsong, J. Tolle and R. Roucka. U.S. Provisional Patent application; filing date 2/12/03. Non-provisional US and PCT patent submitted 3/2004
  - 6 "Direct-gap GeSn, Ge and SiGeSn epilayers and nanostructures grown on silicon", J. Kouvetakis, I.S.T. Tsong, M. Bauer, C.-W. Hu, J. Tolle and J. Menendez. U.S. Provisional Patent application; filing date 6/13/03.
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### Completed Ph.D. and MS Dissertations

1. Jennifer Taraci, **Ph.D** Chemistry, December 2002, "New semiconductor heterostructures and nanostructures in the C-Si-Ge-Sn system".
2. John Tolle, **Ph.D** Chemistry, February 2003, "Growth of wide band gap optical semiconductors on Si via novel Si-Al-O-N and metal boride interfaces".
3. Matthew Bauer, **Ph.D** Chemistry, May 2003, "Si-Ge-Sn semiconductors: new materials with tunable direct band gaps".
4. Cole Ritter, **Ph.D** Chemistry, Fall 2003, "I. Synthesis of main group C-N materials in the Li-Be-B-Mg-Al system. II. Synthesis of group IV hydrides and alloys".
5. Levi Torrison **Ph.D.** Chemistry Fall 2003. "Si-based nanostructures and dielectrics".
6. Candi Cook **MS**, Fall 2003 [Science and Engineering of Materials, (SEM)] "Optical characterization of group IV heterostructures based on silicon germanium and tin"



**Figure 1** a,b: RBS spectra of two representative SnGe/Si films demonstrating full Sn substitutionality. c: high-resolution electron micrograph of interface region. Arrows show misfit dislocations, d: electron micrograph showing film surface, e, selected-area diffraction pattern.



**Figure 2.** Second derivative of the dielectric function for ellipsometric measurements. The direct bandgap for  $\text{Sn}_{0.02}\text{Ge}_{0.98}$  and  $\text{Sn}_{0.14}\text{Ge}_{0.86}$  are 0.74 eV and 0.41 eV respectively, compared to 0.81 eV for Ge.

## Summary of Most Important Results

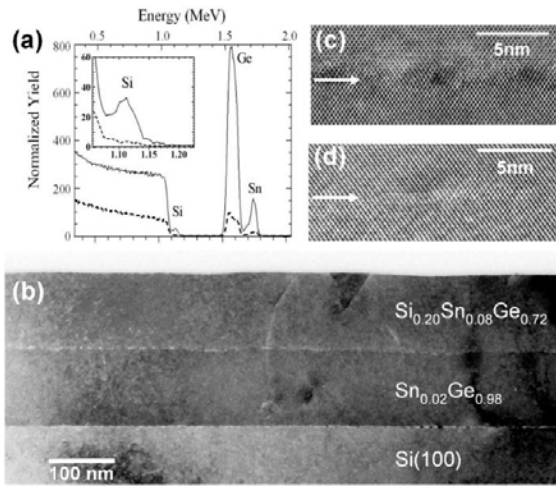
### Si-Ge-Sn alloys grown on Si(100)

Silicon is the most desirable substrate for the growth of semiconductor materials. Virtually defect-free Si wafers are available at low cost, and the range of applications of any semiconductor grown on Si can be enhanced by integration with silicon-based microelectronics. Unfortunately, the growth of semiconductors on Si is fraught with difficulties. A high quality interface between Si and a direct-gap semiconductor, the key component of any device that integrates optoelectronics with microelectronics, has yet to be demonstrated. Excellent quality  $\text{Si}_{1-x}\text{Ge}_x$  alloys can be grown on Si, but the large lattice mismatch between Ge and Si limits considerably the range of Ge-concentrations that can be used.

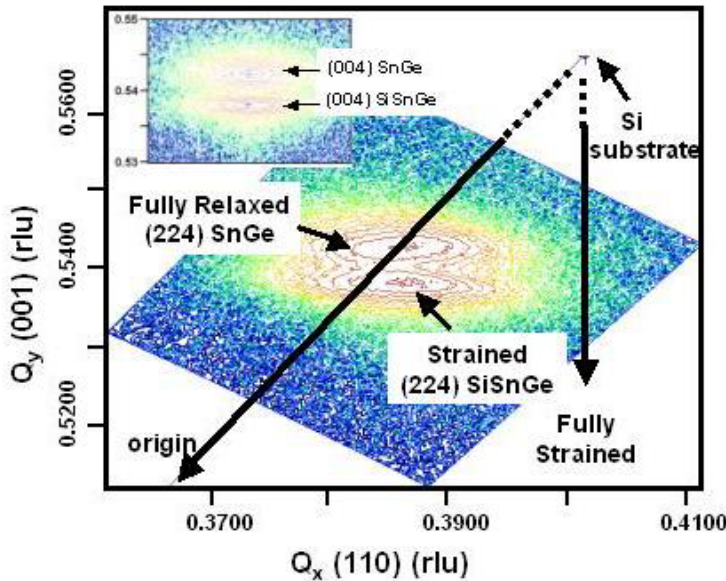
In this report we describe fabrication and optical properties of device-quality, strain-free  $\text{Sn}_x\text{Ge}_{1-x}$  layers grown directly on Si wafers. This is an important development for several reasons. First,  $\text{Sn}_x\text{Ge}_{1-x}$  alloys have been predicted to undergo a transition from indirect- to direct-gap semiconductors so that this material may lead to the first direct-gap semiconductor fully integrated with Si technology. Second, device-quality  $\text{Sn}_x\text{Ge}_{1-x}$  layers of arbitrary thickness can be deposited on Si, and these can be used as "virtual substrates" for the growth of  $\text{Sn}_x\text{Ge}_{1-x}$  alloys of different composition as well as  $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$  ternary analogs. The fabrication of  $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$  makes it possible to decouple strain and band gap engineering to achieve unique devices structures that lead to novel photonic devices based entirely on group IV materials. These systems cover a wide range of operating wavelengths in the IR and include strain-engineered direct gap heterodiodes and multi-quantum well lasers, photodetectors, emitters and modulators grown on  $\text{Sn}_{1-x}\text{Ge}_x$  and  $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$  buffered Si.

**The Ge-Sn system** The  $\text{Sn}_x\text{Ge}_{1-x}$  alloys are grown by a specially developed UHV-CVD method, which is based on reactions between  $\text{SnD}_4$  and  $\text{Ge}_2\text{H}_6$  (digermane). Depositions were conducted in a custom-built ultra-high- vacuum CVD reactor on Si(001) wafers. Growth temperatures between 250° and 350° produced thick films (50-500 nm) with Sn continuous concentrations up to 20 %, as measured by Rutherford backscattering (RBS). Fig 1 (top panels) shows a comparison between random and aligned RBS spectra for a  $\text{Sn}_{0.02}\text{Ge}_{0.98}$  sample and a  $\text{Sn}_{0.14}\text{Ge}_{0.86}$  sample. The ratio  $\chi_{\min}$  between the aligned and random peak heights is 4% in the  $x = 0.02$  sample and about 50% in the  $x = 0.14$  sample for *both* Ge and Sn. This provides unequivocal proof that Sn occupies substitutional sites in the average diamond structure. The  $\chi_{\min} = 4\%$  value closely approaches the practical limit of about 3% for structurally perfect Si, which is unprecedented for a binary crystal grown directly on Si. The structural properties of the films were further investigated by XTEM. Electron micrographs demonstrating nearly defect-free growth of  $\text{Sn}_{0.02}\text{Ge}_{0.98}$  are shown in the bottom panels of Fig. 1. The images show that the predominant defects accommodating the large misfit between the alloys and the Si substrate are Lomer edge dislocations at the interface. These are parallel to the interface plane and do not degrade the film quality. The surfaces are very smooth,, and atomically flat. Electron and X-ray diffraction experiments show a monotonically increasing average lattice constant as a function of the Sn-concentration, with no evidence for a significant tetragonal distortion.





**Figure 3-** (a) RBS aligned (dotted line) and random (solid line) spectra of  $\text{Si}_{0.20}\text{Sn}_{0.08}\text{Ge}_{0.72}$  epilayer and  $\text{Sn}_{0.02}\text{Ge}_{0.98}$  buffer layer showing a highly aligned heterostructure. Inset: magnified view of the Si peak indicating complete substitutionality of Si in the Sn-Ge lattice. (b) XTEM of the entire heterostructure, (c) Si/ $\text{Sn}_{0.02}\text{Ge}_{0.98}$  interface (indicated by arrow) (d)  $\text{Si}_{0.20}\text{Sn}_{0.08}\text{Ge}_{0.72}$ / $\text{Sn}_{0.02}\text{Ge}_{0.98}$  interface.



**Figure 4** Reciprocal space map (RSM) of a  $\text{Si}_{0.20}\text{Ge}_{0.70}\text{Sn}_{0.10}$  sample grown on Si (001) using a GeSn buffer layer, showing the Si, GeSn, and SiGeSn (224) Bragg reflections in absolute reciprocal space units (rlu).  $Q_y(001)=2\lambda/c$ , where  $\lambda=1.54 \text{ \AA}$  is the Cu  $K_\alpha$  and  $c$  the vertical lattice parameter. This gives  $c_{\text{SiGeSn}}=5.728 \text{ \AA}$  and  $c_{\text{GeSn}}=5.681 \text{ \AA}$ . The corresponding in-plane lattice parameters  $a$  for GeSn and SiGeSn are virtually identical and equal to  $5.662 \text{ \AA}$ . The corresponding (004) RSM is shown in the inset. For full relaxation, an epilayer peak lies on a line connecting the Si (224) substrate peak to the reciprocal space origin. **The data show that this line passes through the center of the GeSn peak, consistent with fully relaxed GeSn on Si.** (If the GeSn epilayer were fully strained with its lattice planes aligned with the substrate, it would appear on a vertical line relative to the substrate as shown.) **Note that the SiGeSn layer falls directly below the GeSn buffer indicating that its in-plane lattice constant matches that of GeSn. The SiGeSn film is therefore fully strained with respect to the GeSn buffer layer.**

The optical properties were investigated with infrared spectroscopic ellipsometry. Figure 2 displays the second derivative with respect to energy of the imaginary part of the dielectric function showing that the direct band gap ( $E_0$ ) for samples containing 2 at % and 14 at % Sn are 0.72 eV to 0.41 eV respectively compared with 0.81 eV for pure Ge. The direct bandgap  $E_0$  is essentially reduced to half of its value in pure Ge for only 14% of Sn in the films. The dramatic reduction in bandgap value indicates that a transition from an indirect to direct bandgap has been achieved.

In conclusion, we have demonstrated a wide tunability of the band structure in SnGe alloys grown on Si. Since our materials grow essentially strain-free, there is in principle no upper limit to the Sn concentration that can be achieved. Thus our approach represents the most straightforward route to direct-gap SnGe alloys and a practical solution to the long-standing problem of growing direct-gap semiconductors on Si. The very large lattice mismatch between our films and the Si substrate opens up intriguing new opportunities for band gap and strain engineering on silicon.

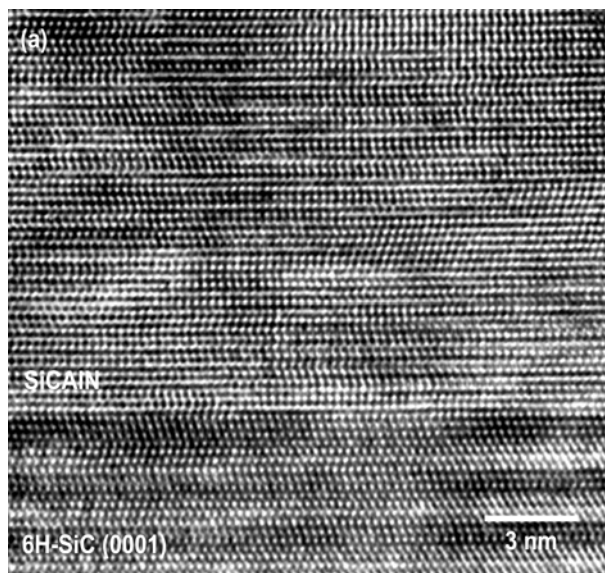
**The Si-Ge-Sn system:** Very recently we have demonstrated growth of device-quality Si-Ge-Sn ternary materials that possess a variable and controllable range of compositions and exhibit lattice constants above and below that of bulk Ge. These materials form more readily and exhibit greater thermal stability than their Sn-Ge counterparts. Combined with the previous demonstration of  $\text{Sn}_x\text{Ge}_{1-x}$  films, the new ternary system provides unprecedented flexibility for band gap and strain engineering in group IV alloys. Possible applications aside from those photonic devices highlighted in the previous sections, include buffer layers for growth of relaxed SiGe alloys with high Ge content and barrier layers for novel type I direct gap Ge quantum wells. We are currently pursuing a vigorous research program in this area to determine the fundamental properties of these materials and to explore practical applications.

The ternaries  $\text{Ge}_{1-x-y}\text{Sn}_x\text{Si}_y$  are grown on Si(100) via  $\text{Ge}_{1-x}\text{Sn}_x$  alloy buffer layers as illustrated by the RBS and TEM data in Figure 3. The crystal structure, elemental distribution and morphological properties of the heterostructures are characterized by high-resolution TEM, including electron energy loss nanospectroscopy, x-ray diffraction and AFM. These techniques demonstrate growth of perfectly epitaxial, uniform and highly aligned layers with atomically smooth surfaces and monocrystalline structures that have lattice constants close to that of Ge. RBS ion channeling shows that the constituent elements occupy random substitutional sites in the same average diamond cubic lattice and the Raman shifts are consistent with the lattice expansion produced by the Sn incorporation into SiGe tetrahedral sites.

The structural and strain properties of these

materials are still virtually unknown and a multidisciplinary effort to determine these is in currently progress. The lattice constant as a function of composition (especially deviations from linearity) and their strain when grown on Si are investigated by high resolution XRD. Figure 4 shows the x-ray reciprocal space map data of a  $\text{Si}_{0.20}\text{Sn}_{0.10}\text{Ge}_{0.70}/\text{Sn}_{0.02}\text{Ge}_{0.98}/\text{Si}(100)$  heterostructure. The data indicate a fully strained SiGeSn epilayer with respect to the relaxed GeSn buffer layer. Related studies show that tensile strained as well as relaxed SiGeSn films can be obtained on strain-free GeSn buffer layers. These results are exciting because they show for the first time that strain engineering can be achieved in SiGeSn heterostructures and multilayers by tuning the lattice parameter of the GeSn buffer layer. A host of novel strained engineered optical and electronic devices have been designed based on this concept. It is interesting to note that the strain is reliably robust up to at least 400-500°C (400°C is the growth temperature of the films).

We have assembled various combinations of concentrations in the Si-Ge-Sn alloy system to form strained-layer



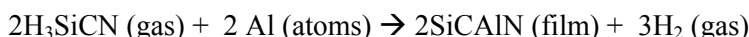
**Figure 5** High resolution image showing epitaxial growth between the wurtzite SiCAIN and the 6H SiC substrate.

heterostructures, such as  $\text{Ge}_{1-x-y}\text{Sn}_x\text{Si}_y$  on  $\text{Ge}_{1-x}\text{Sn}_x$  buffers, where the strain of the ternary can be tuned by adjusting the Si content in the film or the Sn content in the buffer. We have also started the growth of strained Ge films on  $\text{Ge}_{1-x}\text{Sn}_x$  buffers. Theory suggests that tensile Ge layers become direct bandgap materials when the Sn content in the buffer layer exceeds 10 at.%. Other technologically relevant systems we are pursuing include the growth of strained Si on Si-rich  $\text{Si}_y\text{Ge}_{1-y}$ , where the quality of the  $\text{Si}_y\text{Ge}_{1-y}$  buffer is improved through incorporation of a small amount of Sn. Investigations of the thermal stability of these device structures under low-temperature CMOS processing conditions are underway.

### Synthesis and Properties of SiCAIN: A New Wide Bandgap Semiconductor of High Hardness.

SiC and AlN, normally insoluble in each other below 2000 °C, are combined to form single-phase epitaxial layers at 750 °C on 6H SiC (0001). The key to the successful synthesis is the unique combination of a new low-temperature CVD method utilizing a specifically designed unimolecular source  $\text{H}_3\text{SiCN}$  and traditional molecular beam epitaxy of highly reactive fluxes of Al atoms

generated from an effusion cell (see equation below).

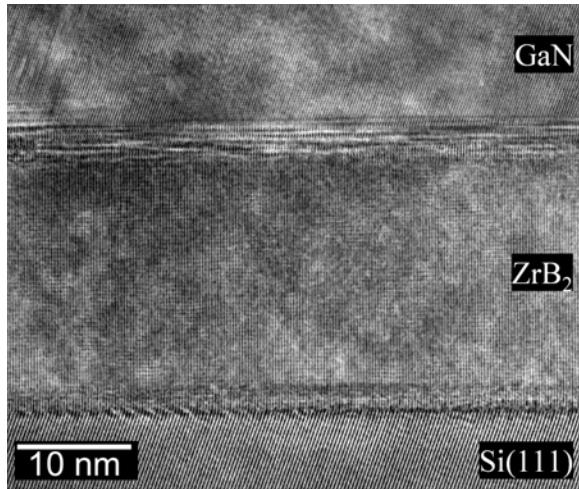


Stoichiometric SiCAIN material is a wide bandgap semiconductor exhibiting luminescence at 390 nm (3.2 eV) consistent with the predicted bandgap of 3.2 eV. Theoretical structural models of the hexagonal SiCAIN agree well with the experimental microstructure observed by cross sectional electron microscopy studies (see figure 5). An average hardness of 25 GPa was measured for SiCAIN, comparable to that measured for bulk sapphire using the nanoindentation method. Growth of single-phase SiCAIN epitaxial films is also conducted directly on Si(111) between 550 and 750 °C despite the structural differences and the large lattice mismatch (19%) between the two materials. Commensurate heteroepitaxy is facilitated by the conversion of native and thermally grown  $\text{SiO}_2$  layers on Si(111) into crystalline oxides by *in situ* reactions of the layers with Al atoms and the  $\text{H}_3\text{SiCN}$  precursor, forming coherent interfaces with the Si substrate and the film. High-resolution transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) show that the amorphous  $\text{SiO}_2$  films are entirely transformed into a crystalline Si-Al-O-N framework in registry with the Si(111) surface. This crystalline interface acts as a template for nucleation and growth of epitaxial SiCAIN. Integration of wide-bandgap semiconductors with Si is readily achieved by this process.

Synthesis of the stoichiometric hybrid SiCAIN is of interest because it combines the novel optical, mechanical, and chemical properties of the binary SiC and AlN constituent systems. Unfortunately the synthetic task is made difficult by the fact that compounds between SiC and AlN can only be made above 1900°C according to the phase diagram using equilibrium methods. Films of  $(\text{SiC})_{1-x}(\text{AlN})_x$  have been previously deposited by MBE and MOCVD at 1200-1300 °C. On account of complexities encountered in the growth process (multiple fluxes, plasmas etc.) as well as the high growth temperatures little progress has been made since these initial studies. Our approach utilizes novel methods and metastable conditions to prepare monocrystalline single-phase SiCAIN at 500-700°C, considerably below the miscibility gap of SiC and AlN. It represents a breakthrough in synthesis of new categories of wide bandgap semiconductors of the main group

and provides a direct way to grow new quaternary materials in the XCZN family, where X is a Group-IV metal and Z is a Group-III metal. Hypothetical semiconductors with adjustable bandgaps, e.g. GeCAIN, are within reach.

## Epitaxial Growth of Tetrahedral Nitrides on Si via a Superhard, Reflective and Lattice-Matched Metal-Boride Buffer Layers



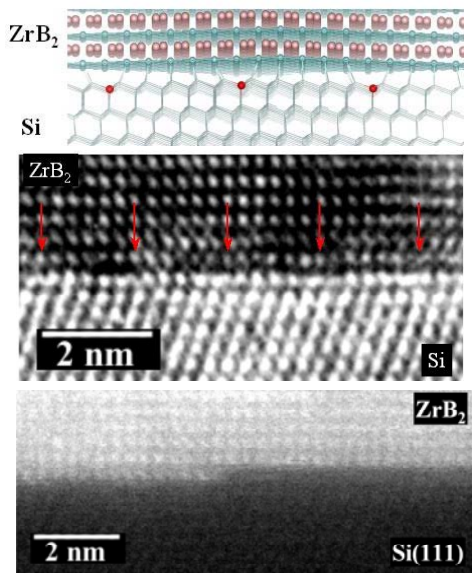
**Figure 6** An XTEM image of a 25 nm thick ZrB<sub>2</sub> grown on Si(111) and a 500 nm thick GaN film grown on ZrB<sub>2</sub>. The epitaxial quality of both ZrB<sub>2</sub> and GaN films is clearly demonstrated.

ZrB<sub>2</sub> has a hexagonal structure with lattice constants  $a = 3.169 \text{ \AA}$  and  $c = 3.530 \text{ \AA}$ . The in-plane lattice constant is less than 2 % with SiCAIN and the optoelectronic nitrides AlN ( $a = 3.11 \text{ \AA}$ ) and GaN ( $a = 3.189 \text{ \AA}$ ). The thermal expansion coefficients along [1010] on the basal plane are also well-matched between ZrB<sub>2</sub> and these materials, particularly GaN. The similarities in structural and thermal properties between ZrB<sub>2</sub> and GaN suggest that ZrB<sub>2</sub>(0001) is an ideal substrate to high quality GaN with low dislocation densities and reduced biaxial strain. Related superhard nitride films of the form SiCAIN, SiCBN, AlB<sub>4</sub>N<sub>2</sub> etc. are likely to grow as epitaxial layers on ZrB<sub>2</sub> buffer layers. Here we describe a method to produce for the first time single-crystalline and perfectly epitaxial ZrB<sub>2</sub> buffer layers on Si(111). We show that the ZrB<sub>2</sub>/Si(111) serves as a ideal template for growth high optical quality GaN and SiCAIN films. Ongoing experiments are focused on development of the isostructural ternary borides Al<sub>1-x</sub>Zr<sub>x</sub>B<sub>2</sub>, Hf<sub>1-x</sub>Zr<sub>x</sub>B<sub>2</sub> and related nitride derivatives in the Al-B-N, Al-Ga-N and Hf-B-N etc. systems. These materials are highly desirable because of their extreme hardness.

The growth of ZrB<sub>2</sub> films on Si(111) substrates at 900°C proceeds via the following reaction:



A typical ZrB<sub>2</sub> buffer layer with a thickness of 50 nm has a metallic appearance and is 100 % reflecting. The surface morphology as shown by AFM and XTEM is virtually atomically flat. X-ray rocking curves indicate high crystal quality.



**Figure 7** (Top) structural model of ZrB<sub>2</sub>/Si interface. (middle) XTEM image of interface. (Bottom) Z-contrast image of interface showing an atomic step. Periodic defects at interface are due to the lattice mismatch (a correspondence of 5 lattice planes of Si to 6 lattice planes ZrB<sub>2</sub> is observed).

Single-crystalline and heteroepitaxial GaN films grown on ZrB<sub>2</sub> at 650 °C display luminescence comparable to those of GaN films grown on sapphire by MOCVD. The microstructure of the GaN/ZrB<sub>2</sub>/Si(111) hetrostructure is shown in XTEM image in Figure 6. Remarkably, in spite of the large mismatch in the in-plane lattice parameter between Si(111) where  $a = 3.84 \text{ \AA}$  and ZrB<sub>2</sub> where  $a = 3.17 \text{ \AA}$ , near-perfect epitaxial growth of ZrB<sub>2</sub> is observed. The misfit at the interface is taken up by a pure edge-type dislocation from the insertion of extra{1100} lattice planes along the [1120] direction. No threading dislocations propagating in a direction normal to the substrate are observed. The ratio of the lattice parameters  $a(\text{Si})/a(\text{ZrB}_2)$  gives 1.21, which translates into an approximate coincidence of 6 ZrB<sub>2</sub> lattice planes with 5 Si lattice planes. The high resolution XTEM image of the interface shown in Figure. 7 shows exactly such a 6:5 coincidence. The occurrence of such a “magic mismatch” between hexagonal ZrB<sub>2</sub> and Si(111) accounts for the epitaxial growth of ZrB<sub>2</sub> even when the lattice mismatch between the two materials is very large. The very sharp transition between Si(111) and ZrB<sub>2</sub>(0001) at the interface is confirmed by the Z-contrast XTEM image shown in Figure 7. In this image, the contrast is a function of the atomic number Z of the element under observation. One can observe that the epitaxy of the ZrB<sub>2</sub> layer is uninterrupted even across an atomic step on the Si(111) substrate.

The ZrB<sub>2</sub> buffer layer on Si(111) provides a near lattice-matched template for the growth of epitaxial GaN. Integration of III-nitrides with silicon electronic circuits is readily achieved. The



reflective nature of the  $\text{ZrB}_2$  surface presents an added bonus to optoelectronic applications of the III-nitrides. Silicon is ~ 45 % absorbing for ultraviolet or near-ultraviolet light. However, with the use of  $\text{ZrB}_2$  buffer layer as a template, the Si(111) substrate becomes 100 % reflecting, thus avoiding any loss of emission intensity from the III-nitrides. The  $\text{ZrB}_2$ /Si(111) substrate offers many distinct advantages in both microelectronic and optoelectronic applications of group III nitrides, the most important of which is the integration with silicon electronics.